DETERMINATIONS OF THE POLLUTION LEVEL OF THE ENVIRONMENT WITH HEAVY METALS

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ABSTRACT: The determination of the pollution level of the environment with heavy metals implies the determination of the metals' concentrations in several samples as much from the point of view of the sample's type as from the point of view of the concentration, which can be situated in domains from ppm order to percentage order. The method of inductively coupled plasma atomic emission spectrometry answers to these requirements, allowing the precise determination in large limits of concentration and in short time.
KEYWORDS: ICP-AES, AAS

1. THE PROPERTIES OF INDUCTIVELY COUPLED PLASMA

The inductively coupled plasma is the spectral source with the largest utilization in the multi-element spectral analyse. Through the inductively coupled plasma atomic emission spectrometry, it is possible to analyse 70 elements at a concentration level of order $ngml^{-1}$.

The main characteristic of the inductively coupled plasma is the gas estate in which a great part of atoms are found in ionized condition, and an interaction of inductive coupling type appears between the plasma and a magnetic field.

The inductively coupled plasma, known under the name of annular discharge, is obtained after ionizing a gas, regularly inert, in an electric field with the frequency of $4 – 50$ MHz and the power in the $1 – 5$ kW domain. The device for producing plasma is named torch; the classic torch for the ICP plasma has three concentric quartz tubes, called exterior tube, intermediary tube and central tube.

At its superior part, the torch is surrounded by an induction bobbin made of copper pipe with two – three helixes, cooled with water and linked to the circuit of radiofrequency of the oscillator. The bobbin develops an oscillating magnetic field whose elliptic shaped lines are oriented axially through the quartz tube. The magnetic field induces in the area of the bobbin an electric field of circular force and oriented perpendicularly on the lines of the magnetic field.

The induced magnetic and electric fields determine a warming of the gas (the argon) to a temperature higher than 5000 K and bring it to plasma estate with an ionizing level of approximately 1%. The Ar^+ electrons and ions thus formed make rotation movements in the induction area following the trajectory of the electric field's lines, producing circular turbine-shaped currents. Through the inferior part of the tube, a flux of argon is introduced, which, at the temperature of the ambient, is an electric isolator. Thus, the free electrons necessary for the appearance of plasma come either from warming up a graphite stick in the induction area, or from some Tesla electric discharges produced in the gas.

Under the influence of the axial magnetic fields, a defined trajectory under the form of a vortex is transmitted to the electrons and ions from the interior of the tube. Because the magnetic fields are variable as power and as direction, the electrons and ions will be accelerated at every half of the period. Through concussions with other atoms, additional ionizing is produced and the dimensions of the plasma increase.

Because in the area of the vortexes the temperatures are of 9000 – 10000 K, the problem of thermo isolation of the plasma appears, in order to prevent the heat losses in the exterior, by the excessive heating of the quartz tube's walls. This can be realized with a plasma sustaining flux of argon with a debit of 10 – 15 l/min, which circulates tangentially between the exterior tube and the intermediary tube, having an ascending direction. It has the role to cool the quartz tube, to sustain, to stabilize and to centre the plasma in report to the induction bobbin.

In the space between the intermediary tube and the central tube, the optional argon circulates at a debit of 1-3 l/min, this flux of gas being used in the case of introducing organic solutions in the plasma, because it reduces the possibility of solid particles being deposited on the top of the central capillary tube.

The argon of injection and nebulizing sample circulates axially through the central tube and it has the role to introduce the sample in the central channel of the plasma. The consume is of 0,4 – 1,5 l/min, determined by the functioning of the nebulizer.

Due to the use of the two or three gas fluxes in sustaining the plasma, and of the surface effect through which the power of radiofrequency is dissipated in the lateral areas of the discharge, the ICP plasma has an annular shape, being formed of a central colder channel, with a diameter of 0,35 – 1 mm, surrounded by a much hotter plasma. An ICP plasma of annular shape is easy to be obtained at a frequency of 27,12 MHz and a debit of Ar of 11 l/min. The annular shape of the ICP plasma determines the main advantages of the plasma: it allows the penetration of the plasma by the sample introducing gas, the atoms of the sample

are mainly found in the central channel, due to the surface effect, the power dissipated in the plasma is independent of the nature and concentration of the sample in the central channel and this implies a good stability of the emission signal, a stationing time of the sample in the plasma of 20 ms enough for the atomizing – ionizing processes and those of excitation to be very efficient, a low spectral fund, the lack of matrix effects, an insignificant mixing of the plasma sustaining gas and the sample from the central channel, which explains the lack of self-absorption.

The ICP plasmas are divided into two main groups: high power ICP plasmas of N_2 – Ar and low & medium power ICP plasmas of Ar – Ar.

The Ar plasma has an ionizing level of up to 1% which corresponds with an electrons density of $5 \cdot 10^{14} - 5 \cdot 10^{15}$ e/cm^3 and an ionizing temperature of 7300 – 8900 K. The excitation temperature is in the domain 5500 – 7000 K [1]. The density of electrons is maximal at a radial distance of 2 – 4 mm $(2 \cdot 10^{15} - 4 \cdot 10^{15}$ e/cm$^3)$ from the centre of the plasma, and it decreases close to the lateral areas and to the centre, and in the central channel where the sample is introduced, the density of electrons decreases with height. The lower value of the electrons' density in the centre of the plasma $(1 \cdot 10^{15} - 1,5 \cdot 10^{15}$ e/cm$^3)$ is explained by its cooling down due to the sample of aerosol, but the density of electrons is enough to produce a very good excitation of the sample.

At this moment the ICP plasmas are most often operated at frequencies of 27,12 and 40,68 MHz and at powers of 0,6 – 1,8 kW at a coupling efficiency of 50 – 70%, the support gas being the pure spectral Ar [2, 3, 5].

The ICP plasma is the ideal spectral source for spectroscopy and it has the largest utilisation in the analyze of samples through atomic emission spectrometry (ICP-AES). Liquid or solid biological, geological, chemical and environmental samples can be analyzed. The liquid samples are pneumatically sprayed into the plasma and the solid ones can be introduced directly or by ablation with laser, or brought to solution and pneumatically sprayed. The detection limits are at $ng \circ ml^{-1}$ level. The inductively coupled plasma is also a source of ions for the analyse through mass spectrometry, this analyse being characterized by very low detection limits, the lack of spectral interferences and the possibility of the isotopic analyse of the elements. The applications through the atomic fluorescence spectrometry are also very well known, a BAIRD spectrometer allowing the simultaneous analyse of 12 elements.

The ICP analytical systems can easily determine the major elements, the minor ones and the micro-traces from the samples, situations which are often found in the case of environmental samples.

2. EXPERIMENTAL DATA

Heavy metals are found among the main polluting agents of the studied area. Their accumulation and distribution in the soil is determined by factors which characterize the pollution source, the nature of the soil, the local geographic and meteorological factors which contribute to the dispersion of pollutants, and also by the nature of the chemical combinations in which the polluting metal is found.

The heavy metals can get into the soil through mine waters, through residual waters of the preparation factories, through dusts coming from metallurgical factories which process mining concentrates or through the waste dumps of mines and flotation factories.

The soil samples were collected from three points situated on West direction from the main polluting source, from the superficial layer of the soil (table 1) and then, from different depths (table 2). In these tables, Pb, Cu, Zn were determined by the method of inductively coupled plasma atomic emission spectrometry, and in the second case, for comparison, also by the AAS method.

The samples were cleaned from their vegetal layer, dried, calcined and passed into solution. These operations are made by acid disintegration and using a microwave of CEM MDS 2000 type. The solutions were analyzed with a BAIRD ICP 2070 spectrometer.

The preparatory operations consisted in selecting the wave lengths for each element, drawing the calibration curves and optimizing the working conditions, so that the analytical performances can be maximal [4].

Table 1. The concentrations of heavy metals in soils (ppm)

Element	Sample 1 3 km	Sample 2 6 km	Sample 3 9 km
Pb	550,3	471,0	159,7
Cu	322,4	209,1	198,0
Zn	1190,2	309,5	298,4

Table 2. Pb, Cu, Zn concentrations at different depths in soil (ppm)

Sample	Distance (km)	Depth (cm)	Pb		Cu		Zn	
			ICP	AAS	ICP	AAS	ICP	AAS
1		10	511,4	502,3	321,4	302,3	1015	983,5
2	3 V	20	354,2	319,3	219,6	163,2	869,4	729,1
3		30	197,8	124,2	113,4	108,4	639,2	482,9

Analysing the data in the tables and their graphic representation, we find high values of all the concentrations of metals close to the source, which decrease with the increase of distance. In order to appreciate the level of pollution, comparisons are made with the maximum concentrations allowed by the national legislation, which foresees as maximum allowed limits in the soil the 100 ppm for Cu and Pb and the 300 ppm for Zn, limits which are exceeded in every sample.

3. CONCLUSIONS

The analysing method used is advantageous from the point of view of the detection limits and of the possibility of multi-element analyse. It allows the determination with the same precision in large limits of concentration and in short time, for the determination of 12 elements only 8 − 10 minutes being necessary.

Making a comparison of the ICP-AES method with the method of atomic absorption spectrometry (AAS), we find that there is a good concordance among the results obtained in the case of high concentrations, while at low concentrations the values are higher in ICP than in AAS, which is explained by the better excitation conditions in the ICP than in the AAS. The studies made demonstrated the possibility of using the ICP-AES method, with very good results, in studies of pollution and speciation of heavy metals.

4. REFERENCES

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